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Growth of Crystals Out of Silver-Containing Glass under Electron Bombardment

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Needlelike crystals grew from a fresh fragment of a silver-containing sodium silicate glass bombarded with intense electron beams in an electron microscope. When the fragment was allowed to stand under a normal atmospheric condition for a week before subjected to the electron bombardment, a little curved rodlike crystals grew from the glass. Electron bombardment caused the formation of colloidal silver within the rodlike crystals.

I. INTRODUCTION

By transmission electron microscopy of fragments of alkali- and lead- silicate glasses, the authors found that needlelike crystals grew from the glasses when bombarded with intense electron beams.[1,2] The present work deals with observations on crystal growth from a sodium silicate glass containing a small amont of silver using the same method as reported previously.[1,3] Fresh fragments obtained by shattering the glass with a hammer as well as thoses allowed to stand under a normal atmospheric condition for a few weeks were used as the samples.

II. EXPERIMENTAL PROCEDURE

Glasses of the compositions, 25 Na_2O·75 SiO_2·0.5 Ag_2O and 25 Na_2O·75 SiO_2 in mole ratio, were prepared from reagent grade chemicals. The crystal growth from the latter was already reported by the authors,[1,2] and its data were used here for comparison. The method for preparation of fragments <500 A thick of the glasses was the same as that reported previously.[1] The fresh fragments were brought into an electron microscope immediatly after shattering the glasses with a hammer in air. Besides the fresh fragments, those allowed to stand under a normal atmospheric condition (temperature : 25–35°C, humidity : about 60%) were also used as the samples.

III. RESULTS

1. Crystal Growth from Fresh Fragments of the Glasses

Representative electron micrographs illustrating the growth of crystals from the fresh fragments of the 25 Na_2O·75 SiO_2·0.5 Ag_2O glass during electron bombardment are shown in Fig. 1. Similar micrographs were obtained for the 25 Na_2O·75 SiO_2 glass which were shown in Fig. 2 for comparison. For both of the glasses, needlelike crystals

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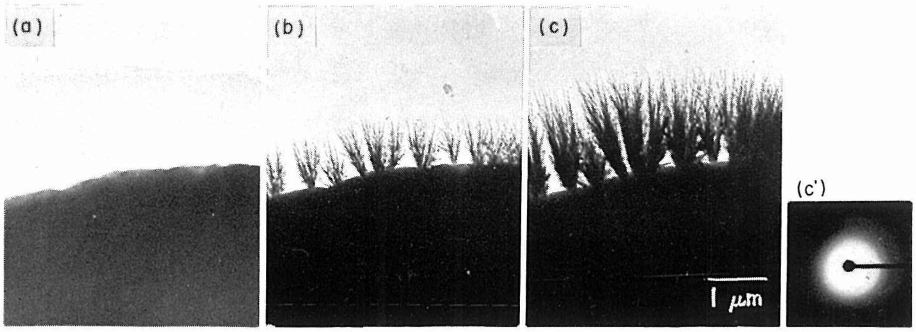


Fig. 1. Crystal growth on surface of 25 Na_2O·75 SiO_2·0.5 Ag_2O glass bombarded with intense electron beams.

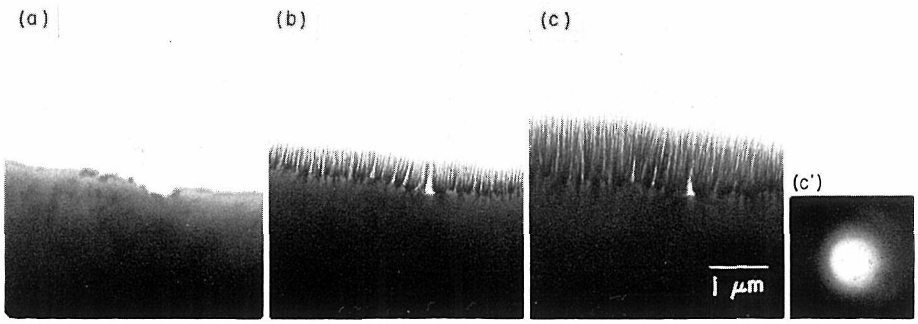
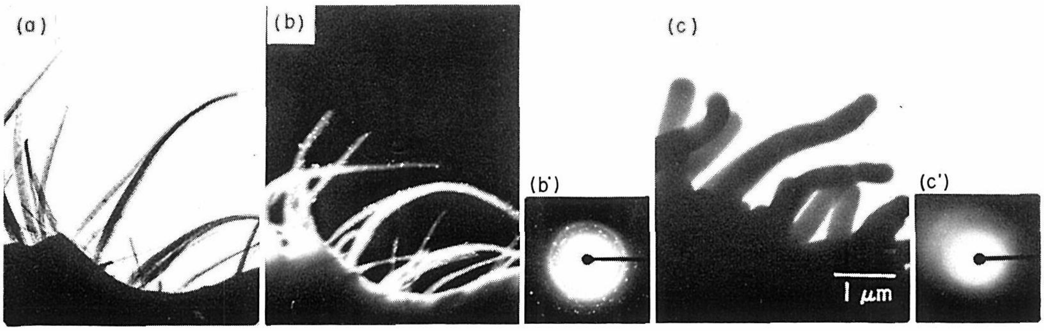


Fig. 2. Crystal growth on surface of 25 Na_2O·75 SiO_2 glass bombarded with intense electron beams.

grew perpendicular to their irradiated surfaces. Their crystal growth rates were almost the same, being 5–15 A/sec. Limited-field electron diffraction patterns of the needlelike crystals grown from both of the glasses were the same (Figs. 1(c′) and 2(c′)).; *i.e.*, they consisted of several diffuse halos and their *d* spacings calculated were 3.0, 2.3, 1.95, and 1.25 A. These facts suggest that the needlelike materials grown from both of the glasses are aggregates of minute crystals of the same kind, probably, consisting of for the most part a sodium compound such as a sodium oxide or sodium carbonate. Presense of crystals having *d* spacings similar to those of a silver metal or of any one of silver compounds could not be confirmed.

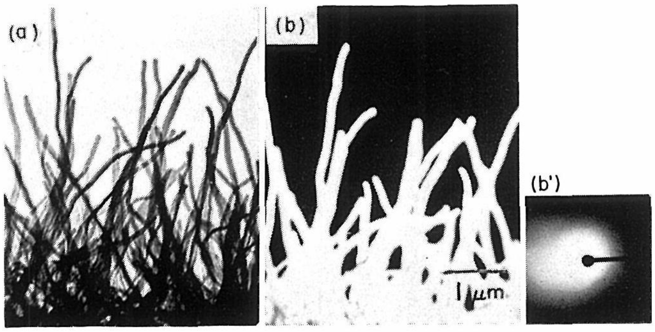
2. Crystal Growth from Glass Fragments Exposed to the Normal Atmosphere for a Few Weeks

Figure 3(a) shows an electron micrographs of rodlike material grown from a fragment of the silver-containing glass which had been kept in the normal atmosphere for a few weeks. This micrograph was taken without bombarding intense electron beams. The diameter of the rodlike crystals formed was about 200 mμ, much larger than that of the needlelike crystals described above. Their shape was not straight but a little curved.



Irradiation 0 min. 2 min. 30 min.
(dark-field)

Fig. 3. Crystal growth on surface of 25 $Na_2O \cdot 75\ SiO_2 \cdot 0.5\ Ag_2O$ glass kept under a normal atmospheric condition for a week.



Irradiation 0 min. 3min.
(dark-field)

Fig. 4. Crystal growth on surface of 25 $Na_2O \cdot 75\ SiO_2$ glass kept under a normal atmospheric condition for a week.

Within the rodlike crystals numerous fine black perticles were observed. When the glass fragment was bombarded with intense electron beams, these particles grew rapidly and started to migrate towards a tip of each rodlike crystal, which could be observed more clearly as numerous bright particles in a dark-field (Fig. 3(b)). The diameter of the particles reached about 30 mμ after the intense electron bombardment for 2 minutes. Figure 3(b′) shows an electron diffraction pattern photographed by focussing an electron beam at the tips of the rodlike crystals. The pattern consisted of many diffuse halos and bright spots indicative of the presence of a silver metal.

Prolonged bombardment with intense electron beams for more than 30 minutes caused the rodlike crystal to grew mostly in diameter (Fig. 3(c)), and at the same time, caused the colloidal silver particles once formed within the rodlike crystals disappear. Figure 3(c′) shows an electron diffraction photograph of the rodlike crystals bombarded with intense electron beams for 30 minutes, in which no bright spots indicative of the presence of silver metal are observed. The halos observed were so diffuse that identification of the rodlike material was unable.

Electron micrographs shown in Fig. 4 illustrate a process of crystal growth from the fragment of the glass containing no silver oxide, which had been kept in the normal atmosphere for a few weeks. A little curved rodlike crystals shown in the photograph of Fig. 4(a) had grown before the fragment was brought into the electron microscope. When the fragment was bombarded with intense electron beams, the rodlike crystals started to grew in diameter in the same way as for the silver-containing glass (Fig. 3(b)). The only difference between the two glasses containing silver and no silver was that no colloidal silver formed within the rodlike crystals grown from the latter glass. Figure 4(b') shows an electron diffraction micrograph of the crystals shown in Fig. 4(b).

IV. DISCUSSION

The mechanism of growth of the needlelike crystals from the fresh 25 $Na_2O \cdot 75\ SiO_2$ glass during intense electron bombardment (Fig. 2) was already explained in the previous report,[1,2] which states that Na^+ ions in the glass move toward the region near the glass surface where high energy electrons entering the glass come to rest. Sodium atoms thus produced form the needlelike crystals either alone or by combining with other available elements such as oxygens.

The needlelike crystals grown from the fresh glass containing silver oxide under the same condition also showed the same appearence under electron microscope and also the same electron diffraction pattern as that of the crystals grown from the glass containing no silver. These facts would indicate that the kinds of the needlelike crystals grown from both of the glasses containing silver and no silver are the same and that the movement of silver ions from their original positions in the silver-containing glass to its surface rich in electrons is much more difficult than that of the sodium ions.

The rodlike crystals grown from the silver-containing glass after kept in the normal atmosphere for a long time had probably been formed by reactions of the sodium and silver ions originally present in the glass with water vapor contained in the atomsphere. It is well known that when a glass is brought into contact with water vapor, mobile ions near the glass surface such as Na^+ and Ag^+ ions are exchanged by protons as expressed by

$$Na^+\,\text{glass} + HOH \longrightarrow H^+\,\text{glass} + Na^+ + OH^-$$

$$Ag^+\,\text{glass} + HOH \longrightarrow H^+\,\text{glass} + Ag^+ + OH^-$$

The Na^+ and Ag^+ ions thus liberated from their original positions can move easily toward the glass surface and there they will form their compounds such as hydroxides, carbonates, or oxides. Some of the silver oxides may dissociate into colloidal silver metal. The rodlike crystals shown in Fig. 3(a) probably consist of such compounds and elements. Rindone already demonstrated that silver films are formed on silver-containing glasses in the presence of water vapor.[4]

When the rodlike crystals described above are bombarded with intense electron beams, dissociation of the silver compounds into silver atoms and further their aggregation will be accelerated. The colloidal silver observed within the rodlike crystals would have formed by such a mechanism. Causes for their movement towards the tip of each rodlike crystal are not clear. It may be caused by ill-balanced electric field produced by electron bombardment in the rodlike crystals. Krauth and Oel[5] found formation of colloidal silver in a silver-containing glass (photochromic glass) by an electron microscopic observation. Although the colloidal silver observed in the present experiment formed within the rodlike crystals protruding from the silver-containing glass, the mechanism of their formation would essentially be the same.

The growth in diameter of the rodlike crystals caused by prolonged electron bombardment would have been caused by transfer of the Na^+ ions from the base glass to the surface of the rodlike crystals. Its mechanism would be the same as in the case of the growth of the needlelike crystals protruding from the fresh glass bombarded with intense electron beams; *i.e.*, the Na^+ ions in the base glass would preferentially be attracted by the surface of the rodlike crystals where high energy electron come to reat during the intense electron bombardment. The diappearence of the bright spots trom the electron diffraction pattern (compare Fig. 3(c′) with Fig. 3(b′)), which resulted from prolonged electron bombardment, was probably caused by either concealment of colloidal silver with sodium compounds piled up on the surface of the rodlike crystals or dissolution of colloidal silver into the pile of the sodium compounds.

V. CONCLUSIONS

When fresh fragments of a silver-containing sodium silicate glass are bombarded with intense electron beams, needlelike crystals, about 10 mμ in diameter, containing sodium ions grow from the glass. If the fragments are allowed to stand under a normal atmospheric condition for a few weeks before subjected to electron bombardment, a little curved rodlike crystals, about 200 mμ in diameter, containing probably sodium ions, and silver ions or atoms are formed, probably, by reactions of their ions with water vapor. When these rodlike crystals are bombarded with intense electron beams, formation of colloidal silver is accelerated within the rodlike crystals. On prolonged electron bombardment, the rodlike crystals continue to grow mostly in diameter while the colloidal silver once formed disappears.

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